

Metallo-Supramolecules: a Study of Structural and Magnetic Properties

T. Geue¹, Y. Bodenthin², U. Pietsch², J. Grenzer², G. Schwarz³, D. G. Kurth^{3,4}, H. Möhwald³

¹Laboratory for Neutron Scattering, ETHZ & PSI, CH-5232 Villigen PSI, Switzerland

²Department of Physics, University Potsdam, D-14415 Potsdam, Germany

³Max Planck Institute of Colloids and Interfaces, D-14424 Potsdam, Germany

⁴National Institute for Materials Science (NIMS) 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

We report on a novel approach to create para- and ferromagnetism in a metallo-supramolecular architecture. In particular, we have investigated thin films of polyelectrolyte-amphiphile-complex containing octahedrally coordinated Fe²⁺ ions showing molecular magnetism above room temperature. Using a combination of magnetic measurements, XMCD and neutron scattering techniques we observed a diamagnetic to paramagnetic phase, which is connected to a phase transition of the amphiphilic layers within the superstructure.

The conversion between a low-spin (LS) and a high-spin (HS) state is typically observed in transition metal ion compounds with a 3dⁿ (4 ≤ n ≤ 7) electronic configuration, the most extensively studied element being the Fe^{II} ion. In a ligand field of octahedral symmetry, the d-orbitals split in 3 low-lying t_{2g} and 2 high-lying e_g levels. Thermal induced spin transitions occur if the energy separation between the t_{2g} and e_g orbitals is approximately equal to k_BT. In the case of the Fe^{II} ion, the LS state arises from a closed-shell t_{2g}⁶ electronic configuration and the HS state from a t_{2g}⁴e_g² electronic configuration, respectively. The spin crossover to the HS state is generally accompanied by a change in optical and magnetic properties, as well as a lengthening of the metal ion–ligand bond due to the occupation of the anti-bonding e_g subset [1].

Two principle strategies have been adopted in ligand design in order to affect the spin state of the coordinating metal ion. The strength of the ligand field can be reduced by steric hindrance in the coordinating ligands, thus, making the HS configuration more favourable [2]. For instance, 2,2':6',2''-terpyridine (tpy) induces a strong ligand field and, therefore, the resulting complexes with iron(II) of the form [Fe(tpy)₂]X₂ are exclusively LS, independent from the counter ion X (Figure 1). While substitution in the 4'-position of the central pyridine ring has no effect, it has recently been recognised that bulky substituents in the 6 and/or 6''-position does affect the spin state [3].

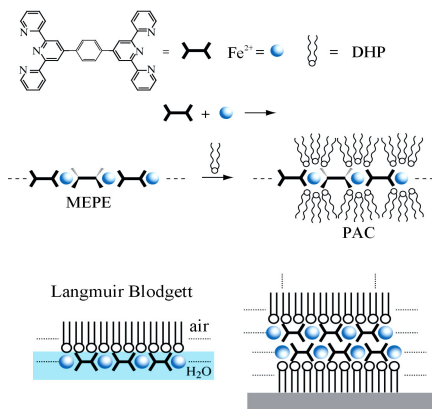


Figure 1: Self-assembly of ditopic bis-terpyridine ligands, transition metal ions and amphiphiles results in polyelectrolyte-amphiphile complexes (PACs). Thin films of PAC were prepared by means of Langmuir-Blodgett technique.

A macroscopic response function of the system, e. g. the magnetisation as a function of temperature, relies on co-operative effects of the individual active centers. In the solid state, co-operativity results from the fact that the equilibrium geometries of the LS and HS states are different and is, therefore, introduced through the degree of interactions between the active centers. We therefore investigated a series of solid PAC samples and solutions in CDCl₃ with different amphiphiles using SANS in a feasibility study. A Porod plot (Figure 2) indicates a more or less distinct grain size distribution and a Bragg peak in low q at 0.0185 Å⁻¹ for the observed series of solid PACs. A number of high q undulations are due to the lamellar structure and the complex molecule shape of the supramolecules. Simulations of these unexpected experimental findings using standard tools weren't successful up to now.

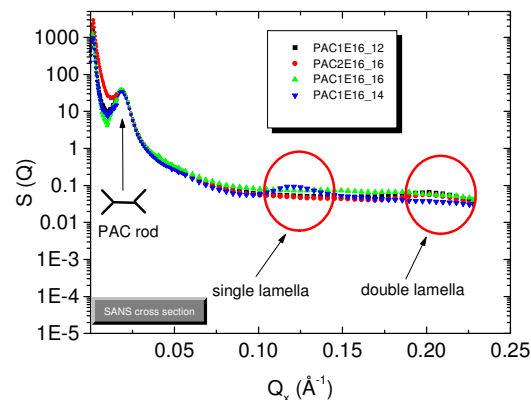


Figure 2: Measured SANS patterns for powder PACs .

The feasibility SANS measurements reveal the validity of the principal approach. A SANS study using polarized neutrons and an external magnetic field should clarify the mechanism of induced paramagnetism in these supramolecular assemblies.

- [1] O. Kahn, C. J. Martinez, *Science* **279** (1998) 44
- [2] Constable E.C. et al. *Chem. Eur. J.* **5** (1999) 498
- [3] Y. Bodenthin, U. Pietsch, J. Grenzer, Th. Geue, H. Möhwald, and D. G. Kurth, *J. Phys. Chem. B* **2005**, submitted

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